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| (21) International Application Number: PCT/US91/08979 (22) International Filing Date: 2 December 1991 (02.12.91) (30) Priority data: 621,313 3 December 1990 (03.12.90) US (71) Applicant: MANVILLE CORPORATION [US/US]; Patent and Licensing Department, P.O. Box 5108, Denver, CO 80217-5108 (US). (72) Inventor: JADA, Sivananda, S. ; 8043 S. Corona Way, Littleton, CO 80122 (US). (74) Agent: QUINN, Cornelius, P.; Manville Corporation, Patent and Licensing Department, P.O. Box 5108, Denver, CO 80217-5108 (US). | | (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: METHOD OF PREPARING CERAMIC HOLLOW PARTICLES (57) Abstract Described is a method of preparing ceramic hollow discrete particles comprising the steps of forming a solution of a silicon containing material at an acidic pH; forming an aqueous ceramic metal oxide precursor solution; forming a homogeneous mixture of the silicon solution and the ceramic metal oxide precursor solution; spray-drying the homogeneous solution by atomizing the solution into a heated chamber having a pressure of at least ambient to form particles; sintering the particles; and recovering silicon metal oxide particles. | | |

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METHOD OF PREPARING CERAMIC HOLLOW PARTICLES

TECHNICAL FIELD

The present invention is concerned with the manufacture of particles in the ceramic field utilizing sol-gel technology.

BACKGROUND ART

U.S. Patent No. 3,709,706 describes refractory aggregates and shaped articles such as fibers, films, flakes and microspheres of zirconia and silica mixtures. Fibers were spun from an aqueous colloidal dispersion of silica and aqueous solution of zirconium diacetate.

U.S. Patent No. 4,349,456 describes shaped and fired porous or impermeable non-vitreous ceramic microcapsules of metal oxide made by a non-melt process comprising the liquid extraction of aqueous metal oxide precursor with a dehydrating liquid having a limited water solubility and drying and firing the resulting gelled microcapsules.

U.S. Patent No. 4,931,414 describes solid transparent non-vitreous microspheres (zirconia-silica) are formed by a extractive gelation (extracting carboxylic acid away from zirconyl carboxylate) of a sol in liquid medium such as hot peanut oil.

It is an object of the present invention to define an improved process to obtain hollow discrete ceramic particles obtained by acidic modification of a

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solution of the reagents prior to formation of the particulates.

It is also an object of the present invention to define an improved process to produce hollow discrete particulates of ceramic materials after the ph adjustment to form the particles by low temperature techniques thereby resulting in energy saving techniques.

It is a further object of the invention to define an improved process to form zircon hollow particulates by drying a ph adjusted solution of the reagents.

SUMMARY OF THE INVENTION

The invention is concerned with the process of preparing ceramic hollow discrete particles comprising the steps:

- 15 (a) forming a solution of a silicon containing material at an acidic ph;
- (b) forming an aqueous ceramic metal oxide precursor solution;
- (c) forming a homogeneous mixture of the silicon solution and the ceramic metal oxide precursor solution;
- 20 (d) spray-drying the homogeneous solution by atomizing the solution into a heated chamber having a pressure of at least ambient to form particles;
- 25 (e) sintering the particles; and
- (f) recovering silicon metal oxide containing particles.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a schematic diagram of the overall process of the present invention to produce the spherical particles;

5 FIGURE 2 shows zircon hollow spheres at 1000 magnification; and

FIGURE 3 is an X-ray diffraction pattern of zircon hollow particles calcined at 1100°C.

DESCRIPTION OF PREFERRED EMBODIMENTS

10 The present invention is concerned with obtaining hollow discrete particles of ceramic materials. One of the initial steps is to prepare a silicon containing aqueous material. The silicon that may be employed can generally be characterized as silicon
15 oxides or alkoxides. The silicon oxides can be silicon dioxide or polymers thereof. The silicon alkoxides can be those comprised of the silicon containing materials further comprising hydrocarbyl containing lower alkyl radicals from 1 to 6 carbon atoms, preferably ethyl.
20 Illustrative materials are tetramethoxysilane, tetraethoxysilane, methyltrimethoxysilane, ethyltriethoxysilane and amyltriethoxysilane, and the like.

 It is most preferred that the silicon material be colloidal silica which has an acidic ph, preferably
25 a ph of 3-5. The colloidal silica is preferably in an aqueous state with a particle size less than 50 nanometers, preferably 0.5-25 nanometers.

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The pH is adjusted from the normal pH of colloidal silica which is basic, usually about 8 to 10 by the use of acidic materials. Any acidic material that does not interfere with subsequent processing steps may be employed whether it be organic or inorganic, although preferably organic acids of less than 6 carbon atoms and even more preferably acetic acid is employed.

To the aqueous colloidal silica solution is added the metal oxide precursor solution. Alternatively, the metal oxide can be placed into an aqueous solution and then the two solutions blended to give a homogeneous solution. The metal oxide can be a dispersion or solution of one or more ceramic metal oxides which include zirconium oxide, TiO_2 , Cr_2O_3 , WO_3 , ThO_2 , Fe_2O_3 , MgO , Y_2O_3 , ZrO_2 , HfO_2 , V_2O_5 , Nb_2O_5 , UO_2 , BeO , CoO , NiO , CuO , ZnO , In_2O_3 , Sb_2O_3 , Al_2O_3 , SnO_2 , and mixtures thereof such as ZnO--TiO_2 , $\text{TiO}_2\text{--Fe}_2\text{O}_3$, $\text{SnO}_2\text{--TiO}_2$, $\text{Nd}_2\text{O}_3\text{--TiO}_2$, $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3$, $\text{MgO--Al}_2\text{O}_3$, MgO--TiO_2 , MgO--ZrO_2 , $\text{ThO}_2\text{--UO}_2$, $\text{ThO}_2\text{--CeO}_2$, $\text{Bi}_2\text{O}_3\text{--TiO}_2$, $\text{BeO--Al}_2\text{O}_3$, $\text{TiO}_2\text{--Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--Fe}_2\text{O}_3$, $\text{PbO--ZrO}_2\text{--TiO}_2$, $\text{ZnO--Al}_2\text{O}_3\text{--Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--TiO}_2$, and $\text{ThO}_2\text{--Al}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--TiO}_2$. It is also within the scope of this invention to use dispersion or sols of said ceramic metal oxides in combination or admixture with dispersions or sols of one or more metal oxides which are unstable in normal air environment (such as Li_2O , Na_2O , K_2O , CaO , SrO , and BaO) and/or ceramic nonmetal oxides having an atomic number of 14 or greater (such as SiO_2 , As_2O_3 , and P_2O_5), representative combinations including $\text{Al}_2\text{O}_3\text{--Li}_2\text{O}$, $\text{TiO}_2\text{--K}_2\text{O}$, $\text{ZrO}_2\text{--CaO}$, $\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--CaO}$, $\text{ZrO}_2\text{--SrO}$, $\text{TiO}_2\text{--BaO}$, $\text{TiO}_2\text{--ZrO}_2\text{--BaO}$, $\text{Al}_2\text{O}_3\text{--Na}_2\text{O}$, MgO--SiO_2 , $\text{Fe}_2\text{O}_3\text{--BaO}$, $\text{ZrO}_2\text{--SiO}_2$, $\text{Al}_2\text{O}_3\text{--As}_2\text{O}_3$, $\text{ZrO}_2\text{--P}_2\text{O}_5$, $\text{Al}_2\text{O}_3\text{--SiO}_2$, $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2$, $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--SiO}_2$. It is preferred that the metal

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oxide is selected from Periodic Table Group II or Group III metals.

A number of the above-described oxides useful in this invention are commercially available in the form of aqueous sols or dry powders which can be readily dispersed in water to form sols, such as Al_2O_3 , Cr_2O_3 and Fe_2O_3 sols sold under the trademark "Nalco", silica sols sold under the trademarks "Nalco," "Ludox," "Syton" and "Nyacol," and Al_2O_3 colloidal powder sold under the trademark "Dispall."

Instead of using the precursor material in the form of dispersion or sols of said oxides, it is within the scope of this invention to use the precursor material in the form of water soluble or dispersible inorganic or organic compounds which are calcinable to the corresponding oxide. These compounds representatively include many carboxylates and alcoholates, e.g. acetates, formates, oxalates, lactates, propylates, citrates, and acetylacetonates, and salts of mineral acids, e.g., bromides, chlorides, chlorates, nitrates, sulfates, and phosphates, selection of the particular precursor compound being dictated by availability and ease of handling. Representative precursor compounds useful in this invention include ferric chloride or nitrate, chromium chloride, cobalt nitrate, nickel chloride, copper nitrate, zinc chloride or carbonate, lithium propylate, sodium carbonate or oxalate, potassium chloride, beryllium chloride, magnesium acetate, calcium lactate, strontium nitrate, barium acetate, yttrium bromide, zirconium acetate, hafnium oxychloride, vanadium chloride, ammonium tungstate, aluminum chloride, indium iodide, titanium acetylacetonate, stannic sulfate, lead formate, antimony chloride, bismuth

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nitrate, neodymium chloride, phosphoric acid, cerium nitrate, uranium nitrate, and thorium nitrate.

It is preferred that the colloidal silica be a very fine particle size. The silica concentration should be less than 50% and preferably approximately 10-30%, and even more preferably, about 20% by weight. The purpose in adding the acidic material is to produce a negative electrostatic charge on the silica particles. Colloidal silica particles exhibit a significant negative electrostatic charge in the ph range of from 3 to 5 and a value within this range is selected for matching with the ph of the aqueous metal oxide solution.

The ph adjusted colloidal silica solution are added to the slurry containing the metal oxide precursor solution and the mixture is stirred, preferably in the presence of ultrasonic treatment to facilitate the reaction. The colloidal silica particles with a negative electrostatic charge are attracted to the positively charged metal ion (for example the zeta potential for zirconia at a ph of 3-5 is approximately 58-64 millivolts).

It is preferred that the ratio of silicon material to metal oxide is from 0.5 to 1.1 (silicon calculated as silicon dioxide) to 1 (metal oxide calculated as metal dioxide) mole ratio. Most preferably, the mole ratio is 1:1.

It is also desirable to prepare a mullite composition, i.e., a metal oxide system that corresponds to three moles of Al_2O_3 to two moles of SiO_2 .

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When ultrasonic treatment is utilized, the processing parameters are at ambient temperature and pressure and that the number of kilohertz ranges from 0.1 to 1 kilohertz, preferably less than 0.1 kilohertz, e.g. 0.05 to 0.07 kilohertz.

After the silicon containing material and metal oxide containing material are blended together in a homogeneous mixture, the concentration ranges from 10 to 60 wt%. The viscosity of the solution ranges from 1 to 40 Centipoise (CPS). Thereafter, the solution or mixture of materials which approaches the gel state is spray-dried into hollow ceramic microspheres in the equipment described below.

After the spray-drying, the particles are subjected to a sintering or calcining treatment to obtain the desired ceramic particles. Preferably, the sintering temperature is at least 250° to 1500°, and even more preferably, about 900° to 1200°Centigrade.

A description of the equipment utilized is as follows:

Figure 1 shows the schematic diagram of the apparatus useful in the present invention. In a tank 10 is a reservoir of the aqueous liquid 12. The tank is open to the atmosphere at the top as indicated by arrows 14. The tank is operated at ambient pressure. A second tank 16 is one that likewise contains liquid 12 which passes from the tank 10 to the tank 16 by pipe 17. The cavity 20 is one that is exposed to atmospheric pressure, for it is the cavity above the reservoir in the tank 10. A similar cavity 22 is atop the reservoir 12 above the level 24 of the fluid in the reservoir 16.

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The lower tank 16 likewise is open to the atmosphere as is indicated by arrow 26. Line 18 maintains equal pressure in tanks 10 and 16. The liquid transfer tube 28 is attached to nozzle means generally shown as reference numeral 30. The inlet 32 for the liquid is placed adjacent to the air inlet 34 which is connected to an air pump generally expressed as 36. The nozzle 30 is generally available from Spraying Systems, Inc. of Wheaton, Illinois, and is utilized in this invention as follows. When air from pump 36 passes through conduit 34 and air outlet 38, the liquid composition from reservoirs 12 and 24 pass through conduit 32 and is atomized into heated chamber 40. The spray nozzle 30 is locked in position by lock nut 42 onto an appropriately configured vessel 44. The top portion 46 of the nozzle is appropriately configured to lock in place at position 48 which is at the bottom of container 40. The spray 50 from the air pump is schematically shown in Figure 1. When the liquid passes through the air nozzle, an atomized spray occurs whereby particulates are formed and subsequently become hollow spheres as the aqueous portion of the mixture is volatilized off in the heated chamber 40. The particles are subsequently collected at a trough at the bottom (not shown) and the volatilized portion of the aqueous material is disposed of (apparatus not shown).

As the aqueous medium 24 is pulled by vacuum through line 32 and corresponding conduit 28, the reservoir level 24 drops. In order to maintain equal atmospheric pressure in spaces 20 and 22, the liquid 12 flows through pipe 17 into container 16 thereby increasing the level 24 to the point that it is just at the exit 52 of conduit 18.

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The orifice 38 is preferably 0.016 inches in diameter and the orifice 33 of conduit 32, ranges from 0.05 inches for the inner diameter to 0.064 inches for the outer diameter or .007 inches. The air is fed through conduit 34 at a range of 5 to 100 pounds per square inch gauge (psig), and even more preferably, 10 to 70 psig, most preferably, 15 to 30 psig.

Two of the interior walls of heat chamber 40 have four 500 watt strip heaters attached to black painted aluminum plates attached to the interior of the walls of the reservoir 40. The heating of the chamber preferably exceeds 250°F, and even more preferably, 400° - 1000°F. When the aqueous composition was atomized into the container, the non-spraying temperature would drop a minimum of 100°F during spraying.

The microspheres or particles that are produced preferably have a size less than 75 microns with a lower limit of approximately 1 micron. The size range is preferably 10 to 60 microns, and even more preferably, 15 to 50 microns.

It is to be appreciated that particles that are not hollow may be produced, although that is not the preferred product. This may be accomplished by modifying the processing conditions such as a lower drying temperature and a higher viscosity homogeneous solution that is spray-dried.

It is to be appreciated that an alternative particle collection device can be anything commercially available such as a cyclone collection system with a separate system for separating and collating the particulates depending upon the sizes desired for particles.

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The microspheres preferably will have a surface area greater than 75 square meters (m^2) per gram, preferably 150 square meters per gram and upwards of 250 square meters per gram.

5 Having the described the invention in general, listed below are descriptions of preferred embodiments wherein all parts are parts by weight, all temperatures are degrees Centigrade, unless otherwise indicated.

Example 1

10 Colloidal silica (LudoxTM, trademark of E.I. DuPont Company) having an average particle diameter 7 nanometers with a ph of 9.9 is diluted with water to make a 21% by weight percent silica in the mixture. After dilution and stirring of the mixture, the ph of
15 the solution is adjusted to a ph in range of 3 to 5 by the addition of acetic acid. A second slurry was prepared of zirconium acetate (21% by weight) which is stirred. The ph adjusted colloidal silica solution is then added to the slurry containing zirconium acetate
20 and stirred in the presence of ultrasonic equipment operating at 60 - hertz. The $SiO_2:ZrO_2$ is a 1:1 mole ratio. After a period of time, the viscosity of the mixture was 4-5 CPS. The mixture was then placed in a piece of equipment comparable to that shown in Figure 1.
25 Air was pumped through nozzle 34 with the aqueous liquid being sucked through conduit 32 and likewise through conduit 28 from reservoir 12 and vessels 16 and 18. The temperature of the vessel 40 was initially 400°F and during spraying decreased to approximately 275° to
30 300°F. The particles were collected at the bottom and were subjected to sintering or drying. The particles were dried for 2 hours at 250° then at 650° for 2-4

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hours until the powder is colorless and then for 2 hours at 1100°C. The X-ray diffractogram of the sample calcined to 1100°C is shown in Figure 3. X-ray diffraction pattern of zirconium silicate, zircon, (ZrSiO₄), matches standard pattern PDF file No. 6-266, JCPDS International Center for Powder Diffraction Data except for two weak diffraction peaks. Figures 2-3 clearly demonstrate that pure zircon hollow particles have been produced. The hollow spheres, approximately 10-20 microns in diameter, are tough, dimensionally stable over a range of temperatures up to 2500°C.

The sample produced was tested at 500°F using the guarded hot plate method where the density was 75 pounds per cubic foot having a thermal conductivity of 1.86 (btu-inches per hour - per square foot per degree Fahrenheit). Comparable experiments were conducted according to ASTM-C 177 for different temperatures ranging from 600°F to 1400°F. The zircon samples were prepared by pouring the zircon material into Ceraboard (trademark of Manville Sales Corporation) rings with a glass cloth top and bottom. After the samples were tested, physical cracks with depths of 0.25+ inches were observed. The results are tabulated below.

| Density | Thermal Conductivity | | | |
|---------|---------------------------------|-----|------|------|
| | (BTU-in/hr-ft ² -°F) | | | |
| (pcf) | 600 | 800 | 1000 | 1400 |
| 51.0 | .65 | .69 | .77 | 1.23 |

Example 2

Colloidal silica, Ludox™ (trademark of DuPont Company) having an average particle diameter of 12 nanometers with a ph of 8.9 is diluted with water to a

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solution that is 21% by weight percent silica. After dilution and stirring of the mixture, the ph of the solution is adjusted to a ph in range of 3 to 5.

5 A second slurry was prepared of zirconium oxychloride (Magnesium Elektron Co.), 21% by weight, which is stirred. The ph adjusted colloidal silica solution is then added to the slurry containing zirconium oxychloride and stirred with a mechanical mixture. The $\text{SiO}_2:\text{ZrO}_2$ is a 1:1 mole ratio. After a period of
10 time, the viscosity of the mixture was 3-5 CPS. The mixture was spray-dried and calcined the precursor hollow microspheres as described in Example 1.

The thermal conductivity (mixture of zircon and fumed silica) results are tabulated below:

| 15 | Density (pcf) | Mean Temp. Degree°F | Apparent Thermal Thermal Conductivity (BTU-IN/HR-FT ² -°F) |
|----|------------------|------------------------|---|
| | 19.3 | 999.6 | 0.29 |

20 Example 3

Hollow microspheres were prepared in the same manner as in Example 1 except that zirconyl oxynitrate [$\text{ZrO}(\text{NO}_3)_2$] is used.

Example 4

25 Hollow microspheres were prepared in the same manner as in Example 1 except that 2% w/w of B_2O_3 by the weight of zircon was added as boric acid to the precursor solution.

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Example 5

In a separate beaker, take Ludox™ 180g and to that add 180g (equal amount) of water. Then add 4-5g of acetic acid. Add this ph adjusted Ludox™ to a solution
5 of 558.1g aluminum oxychloride (50% by wt) in 500 ml ethanol. Mix thoroughly.

The solution was combined up to make approximately 5 gallons of precursor solution.

The solution was spray-dried using the apparatus of Figure 1.
10

The spray-dried material was sintered at 250°C for 1 hour; 650°C for 1 hour and finally at 1000°C for 48 hours. The oven was cooled to room temperature. The products were tested by spectroscopic and X-ray diffraction tests for composition were determined to be mullite particles.
15

Further, the calcined mullite particles were hollow as evidenced by electron micrographs. Analysis of the spray-dried granules is: %C: 2.99; %H : 1.82; %Cl: <0.53; %Al: 27.2; %Si: 18.41.
20

Example 6

Hollow mullite particles were prepared in the same manner as in Example 5 except that % w/w of B₂O₃ by the weight of mullite was added as boric acid to the precursor solution.
25

The compositions herein can be used for insulation purposes and refractory purposes such as

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insulation of heated products or appliances. Other end
uses are thermal shields in space exploration equipment,
missiles, rockets and in commercial and military air-
craft for heat and/or fire protection in voice record
5 box, engine parts, fuselage, and the like.

While the forms of the invention herein
disclosed constitute presently preferred embodiments,
many others are possible. It is not intended herein to
mention all of the possible equivalent forms or ramifi-
10 cations of the invention. It is understood that the
terms used herein are merely descriptive rather than
limiting, and that various changes may be made without
departing from the spirit or scope of the invention.

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WHAT IS CLAIMED IS:

1. A method of preparing hollow discrete particles comprising the steps:

5 (a) forming a solution of a silicon containing material at an acidic ph;

(b) forming an aqueous ceramic metal oxide precursor solution;

10 (c) forming a homogeneous mixture of the silicon solution and the ceramic metal oxide precursor solution;

(d) spray-drying the homogeneous solution by atomizing the solution into a heated chamber at a pressure of at least ambient temperature to form particulates;

15 (e) sintering the particles; and

(f) recovering silicon metal oxide particles.

2. The method of claim 1 wherein the silicon solution of step (a) is colloidal silica with a particle size less than 50 nanometers.

20 3. The method of claim 1 wherein the ph of the solution is adjusted to 3 to 5.

4. The method of claim 1 wherein the metal oxide is zirconia.

25 5. The method of claim 1 wherein the mole ratio of silicon to metal oxide in step (c) ranges from 0.5 to 1.1 moles of silicon (calculated as silicon dioxide) : 1 mole of metal oxide (calculated as metal oxide).

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6. The method of claim 1 wherein the drying of step (d) is conducted at a temperature of 120°C to 200°C.

5 7. The method of claim 1 wherein the sintering of step (e) is conducted at a temperature of 250°C to 1200°C.

8. The method of claim 7 wherein the temperature ranges from 900°C to 1200°C.

10 9. The method of claim 1 wherein hollow zircon particles are produced.

10. The method of claim 8 wherein hollow zircon particles are produced.

11. The method of claim 8 wherein hollow mullite particles are produced.

15 12. The method of claim 1 wherein the metal oxide is selected from the group consisting of Periodic Table Group II or Group III metals.

20 13. The method of claim 1 wherein the viscosity of the composition of step (c) ranges from about 1 to about 40 Centipoise.

14. The method of claim 1 wherein the particles produced range in size from about 0.5 to 100 microns.

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15. A method of preparing discrete particles comprising the steps:

(a) forming a solution of a silicon containing material at an acidic ph;

5 (b) forming an aqueous ceramic metal oxide precursor solution;

(c) forming a homogeneous mixture of the silicon solution and the ceramic metal oxide precursor solution;

10 (d) spray-drying the homogeneous solution by atomizing the solution into a heated chamber at a pressure of at least ambient temperature to form particulates;

(e) sintering the particles; and

15 (f) recovering silicon metal oxide particles.

16. The method of claim 15 wherein the silicon solution of step (a) is colloidal silica with a particle size less than 50 nanometers.

17. The method of claim 15 wherein the ph of
20 the solution is adjusted to 3 to 5.

18. The method of claim 15 wherein the metal oxide is zirconia.

19. The method of claim 15 wherein the mole ratio of silicon to metal oxide in step (c) ranges from
25 0.5 to 1.1 moles of silicon (calculated as silicon dioxide) : 1 mole of metal oxide (calculated as metal oxide).

20. The method of claim 15 wherein the drying of step (d) is conducted at a temperature of 120°C to
30 200°C.

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21. The method of claim 15 wherein the sintering of step (e) is conducted at a temperature of 250°C to 1200°C.

5 22. The method of claim 21 wherein the temperature ranges from 900°C to 1200°C.

23. The method of claim 15 wherein zircon particles are produced.

24. The method of claim 22 wherein zircon particles are produced.

10 25. The method of claim 22 wherein mullite particles are produced.

26. The method of claim 15 wherein the metal oxide is selected from the group consisting of Periodic Table Group II or Group III metals.

15 27. The method of claim 15 wherein the viscosity of the composition of step (c) ranges from about 1 to about 40 Centipoise.

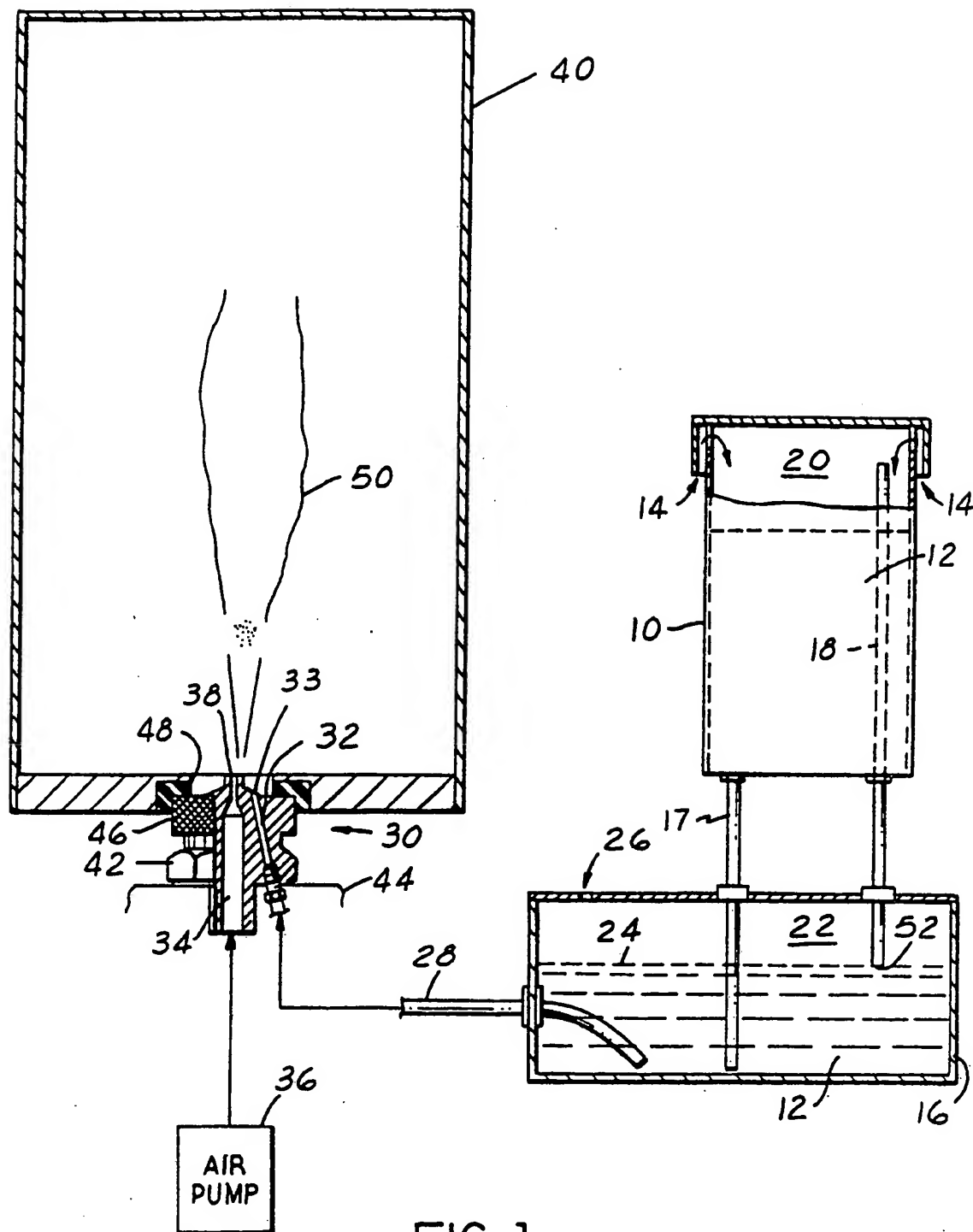
26. The product of the process of claim 1.

27. The product of the process of claim 10.

20 28. The product of the process of claim 15.

29. The product of the process of claim 22.

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FIG. 1

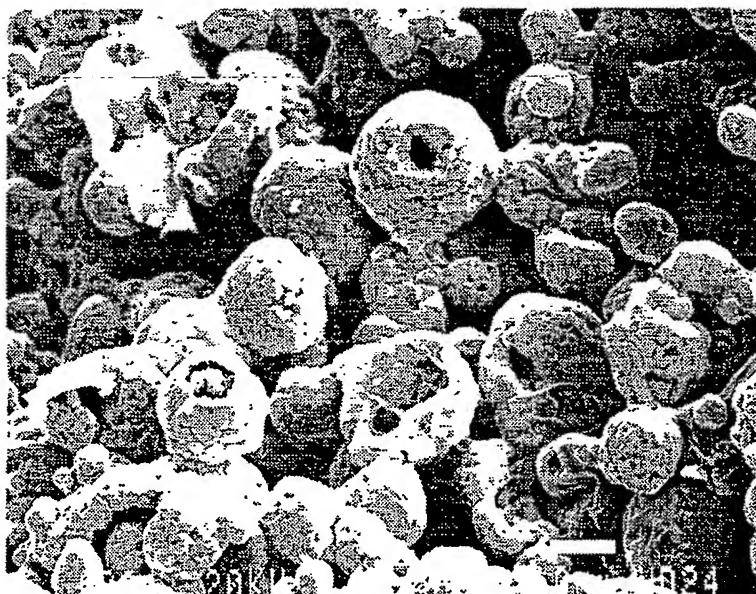


FIG. 2

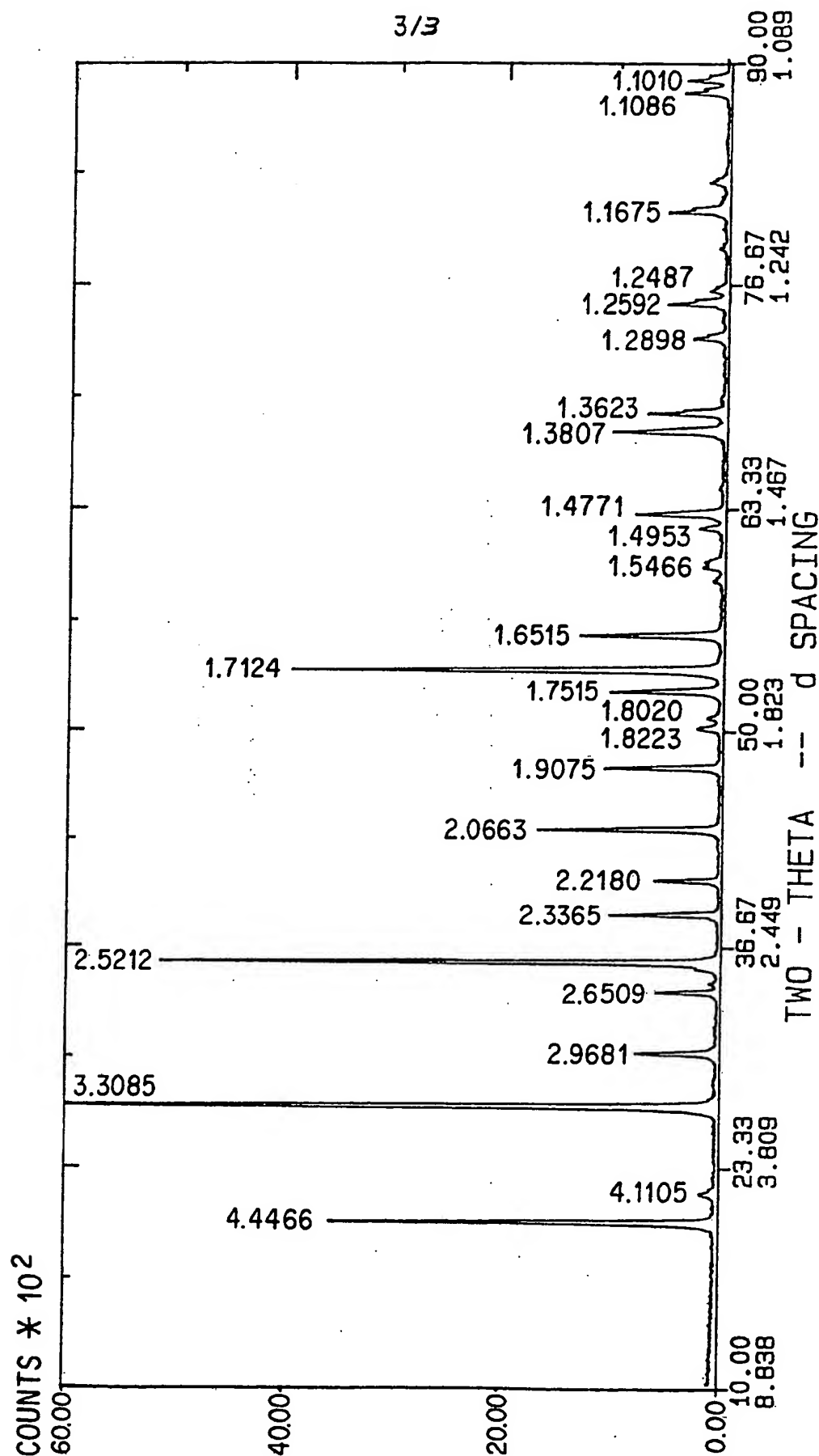


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/08979

| | | |
|--|--|-------------------------------------|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C04B38/00; C01B13/34; C01B33/20; C01B33/26 | | |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁷ | | |
| Classification System | Classification Symbols | |
| Int.Cl. 5 | C01B ; C04B | |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ | | |
| | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ | | |
| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
| X | PATENT ABSTRACTS OF JAPAN vol. 13, no. 466 (C-646)20 October 1989 & JP,A,1 183 403 (IDEMITSU KOSAN CO. LTD, JP) 21 July 1989 see abstract --- | 1,7,14, 15,21, 28,30 |
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| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div> | | |
| IV. CERTIFICATION | | |
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
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